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# Supramolecular fullerene architectures by quadruple hydrogen bonding

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## Abstract

The synthesis and full characterization of a quadruple bonded fullerene dimer using self-complementary 2-ureido-4[1H]-pyrimidinone units with high dimerization constants is described. The chemical integrity of the monomeric moiety in either compound is fully preserved, also with respect to its redox and UV-Vis behavior. Two novel supramolecular dyads consisting of an oligo(*p*-phenylene vinylene) (OPV) donor and fullerene (C<sub>60</sub>) acceptor are created via quadruple hydrogen bonding upon mixing the fullerene dimer and an OPV dimer. In these supramolecular dyads, singlet-energy transfer from the excited OPV unit to the fullerene causes a strong quenching of the OPV fluorescence. The high association constant of the 2-ureido-4[1H]-pyrimidinone quadruple hydrogen-bonding unit results in high quenching factors ( $Q_{\max} \geq 90$ ). The lower limit obtained for the rate constant for energy transfer ( $k_{EN} \geq 6 \times 10^{10} \text{ s}^{-1}$ ) is rationalized in terms of the Förster mechanism.

**Keywords:** Solution self-assembly; IR spectroscopy; NMR spectroscopy; Electrochemical methods; Photoluminescence; Fullerene derivatives.

## 1. Introduction

Fullerenes have interesting properties that may be utilized in a variety of applications including organic photovoltaic (PV) devices [1]. Especially organic bulk-heterojunction PV cells consisting of a blend of a  $\pi$ -conjugated polymer and a fullerene derivative [2] have received much attention recently. A way to improve the efficiency of these so called “plastic” solar cells is the optimization of the morphology of the photoactive layer. A potential way to obtain this goal is through supramolecular assembly of the constituents. Hydrogen bonding is particularly useful in the construction of supramolecular structures [3]. Monofunctionalized C<sub>60</sub> derivatives bearing one or two hydrogen bonding moieties on the substituent can serve as building blocks for the preparation of fullerene-containing dimers and arrays, using the strength,

directionality and specificity, characteristic of hydrogen bonding [3].

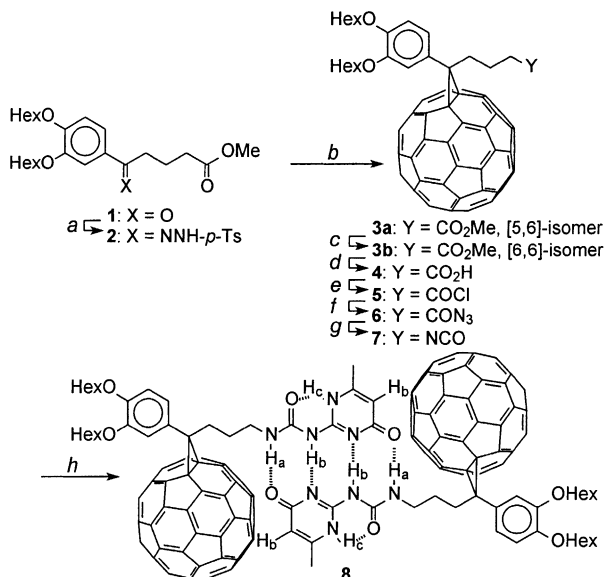
To elucidate the influence of hydrogen bonding interaction on photophysical properties various studies were performed, in which systems containing multiple hydrogen bonds were designed to gain strength and directionality. The 2-ureido-4[1H]-pyrimidinone unit (Fig. 1) is a self-complementary DDAA motif quadruple hydrogen-bonding unit that possesses a high association constant of at least  $6 \times 10^7 \text{ M}^{-1}$  depending on the solvent used [4].

## 2. Results and Discussion

The synthesis of the quadruple hydrogen bonded fullerene dimer **8** is depicted in scheme 1 [5]. The <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> showed the typical resonances for the four dimer bonding hydrogen atoms of **8** at  $\delta$  11.81

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(H<sub>b</sub>) and  $\delta$  10.40 (H<sub>c</sub>), a signal at  $\delta$  12.98 for the intramolecularly bonded H<sub>a</sub>, and one at  $\delta$  5.75 for the vinylic proton H<sub>d</sub> (Sch. 1). No monomer was observed at a concentration of  $1.0 \times 10^{-5}$  thus giving a lowest estimate of the dimerization constant of  $1 \times 10^6$ . <sup>13</sup>C-NMR, UV-Vis, FTIR, and MALDI-TOF supported structure **8**.



Scheme 1. a. p-TsOH, MeOH, 6h.,  $\Delta$ , 61 %; b. 1. NaOMe, py, 30 min., r.t., C<sub>60</sub>, ODCB, 80 – 90 °C, 16 h.; c. ODCB, 500 W flood lamp, 100 min.; d. ODCB, HOAc, HCl, H<sub>2</sub>O, 16 h., 36 % (2 → 4, 3 steps); e. SOCl<sub>2</sub>, CHCl<sub>3</sub>, 1h.; f. NaN<sub>3</sub>, ODCB, DMAC, r.t. 75 min.; g+h. 2-amino-4-hydroxy-6-methylpyrimidin, py, 70 – 80 °C, 2h., 71 % (4 → 8, 3 steps).

Cyclic voltammetry of **8** showed four waves corresponding to reduction of the fullerene core (at -0.68, -1.01, -1.56, and -2.02 vs. Ag wire) as well as a weak wave at -1.84 V and a shoulder at -1.15 V. The latter two waves are related to the 2-ureido-4-pyrimidinone moiety.

The focus of the present study is the formation and excited-state behavior of a quadruple hydrogen bonded dyad involving **8** as the C<sub>60</sub> acceptor and **9** and **10** as the OPV4 donors (Fig. 1) [6].

The high fluorescence quantum yield of the **9** and **10** in solution, together with the strong quadruple hydrogen bond, allows us to investigate photoinduced energy and electron transfer reactions at extremely low concentrations. The combination of a high binding constant and low concentrations in the experiments, minimizes collisional donor-acceptor interactions and the interference of free molecules present in solutions in photophysical experiments. The true (static) properties of the donor-acceptor complex in energy or electron transfer can be studied, since the lifetime of the D-A complexes (>100 ms) is significantly longer than the expected photophysical processes [4].

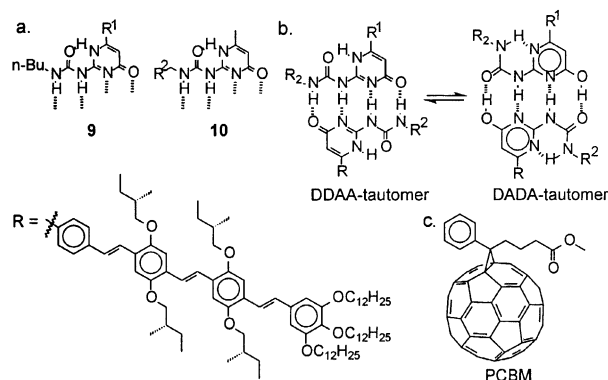


Fig. 1. a. OPV4 donors **9** and **10**; b. DDAA- and DADA tautomers. c. PCBM.

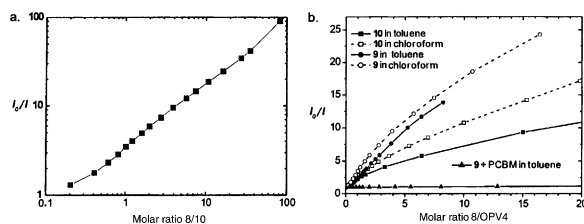
Besides the 2-ureido-4[1H]-pyrimidinone, also referred to as *keto* form (DDAA motif), the pyrimidin-4-ol or *enol* tautomer can be present (DADA motif, fig. 1). An electron withdrawing R<sup>1</sup> substituent stabilizes the *enol* form. Also, more apolar solvents like toluene favor the *enol*-form. The DADA motif has a lower association constant ( $\sim 10^4$  to  $10^5$  M<sup>-1</sup>) [7].

The DDAA and DADA motifs are not complementary and, hence, the equilibrium will affect the formation of the homo- and hetero-dimers. We found that in chloroform, **10** is solely present in the DDAA tautomeric form, while **9** contains some (10–15 %) of the *enol*. In toluene, the amounts of *keto* are less. **10** is for 90 % in the DDAA form in toluene, while the amount of 4[1H]-pyrimidinone in **9** has dropped to 50 %. The <sup>1</sup>H NMR spectrum of **8** in toluene indicates that only the *keto* form is present.

Information on the rate for energy or electron transfer within a hetero-dimer can be obtained by monitoring the quenching factor *Q*, of the OPV4 moiety upon addition of **8** (*I*<sub>0</sub>/*I*; *I*<sub>0</sub>: initial fluorescence OPV4's, *I*: fluorescence after addition of **8**). The results are depicted in a modified Stern-Volmer [8] plot (Fig. 2a). To ensure that only energy transfer occurs from the OPV4 to **8**, rather apolar solvents as toluene and chloroform were used. To avoid contributions of OPV4 fluorescence quenching via collisional quenching and to minimize additional fluorescence from OPV4 monomers, the total concentration of the hydrogen bonding units was kept between 10<sup>-3</sup> and 10<sup>-6</sup> M. A control experiment using **9** and the non-hydrogen bonding soluble PCBM (Fig. 1c) gave no quenching under the experimental conditions (Fig. 2b) proving that collisional quenching is not important at this concentration. Consequently, the observed OPV4 photoluminescence only results from OPV4 homo-dimers and **8**/**9** hetero-dimers. Hence, any quenching (*Q*) observed results from hetero-dimers only.

Fig. 2a shows that indeed a pronounced quenching of the fluorescence of **10** occurs upon addition of **8** to **10** in chloroform due to the supramolecular association between the two moieties [9]. In the case of **8**/**10** in chloroform, a

fluorescence quenching of  $\geq 98.9\%$  is obtained at the highest 8/10 ratios investigated. Interestingly, the  $Q$  value already exceeds the value of 2 at an 8/10 ratio of 1 : 1, which indicated that there is a preference for the heterodimer [10].



**Fig. 2.** a. Modified Stern-Volmer plot for the fluorescence quenching of **10** ( $10^{-6}$  M) in  $\text{CHCl}_3$  upon addition of **8**,  $\lambda_{\text{excit}} = 432$  nm,  $\lambda_{\text{detect.}} = 492$  nm; b. Modified Stern-Volmer plot of fluorescence quenching in PhMe and  $\text{CHCl}_3$ .  $[\text{OPV4}] = 10^{-6}$  M.  $I_0$  is the fluorescence signal of the pure OPV4-UP solution.  $\lambda_{\text{excit}} = 432$  nm,  $\lambda_{\text{detect.}} = \lambda_{\text{max}}$ .

Without knowing the exact amounts present, the non-statistical distribution prevents an accurate estimate of the limiting quenching factor  $Q_{\text{max}}$  of a hetero-dimer. However, a lower limit of  $Q_{\text{max}}$  can be obtained from the amount of fluorescence quenching at large 8/10 ratios ( $> 50$ ), where the excess of **8** causes most of the donor to be attached to an acceptor molecule. In the case of 8/10 in chloroform, this results in  $Q_{\text{max}} \geq 90$ . This lower estimate for  $Q_{\text{max}}$  is more than one order of magnitude larger than quenching factors previously reported for hydrogen-bonded donor-acceptor dyads. Toluene instead of chloroform lowered  $Q$ , which was explained by the diminished coupling in the increased amount of DADA-tautomer of the heterodimer. The rationale that the amount of quenching is proportional to the amount of *keto* form present, is supported by the fluorescence quenching experiments on **9** in chloroform and toluene upon addition of **8**. For **9** the amount of *keto* is much less in toluene than in chloroform (Table 1). Accordingly, the quenching of the fluorescence of **9** in chloroform is almost double to that in toluene.

Table 1. Percentage of 4[1H]-pyrimidinone (% *keto*) determined from  $^1\text{H}$  NMR spectroscopy.

|           | $\text{CHCl}_3$ (% <i>keto</i> ) | toluene (% <i>keto</i> ) |
|-----------|----------------------------------|--------------------------|
| <b>9</b>  | 85 - 90                          | $\sim 50$                |
| <b>10</b> | $> 99$                           | 90                       |

Nevertheless, there is a remarkable difference in the amount of quenching of the OPV4's in both solvents (Fig. 2). Even in chloroform, where the *keto* form is the dominant tautomer, the fluorescence of **10** is quenched to a significantly larger extent than that of **9** upon adding **8**.

The fluorescence quenching experiments of the **9** and **10** using **8** afford the quenching factors at different ratios of

quencher versus fluorophore. We have shown that these values are directly related to the dimerization equilibrium of the hydrogen bonding molecules, their opportunity to form hetero- or homo-couples and the *keto-enol* equilibrium of the individual chromophores.

Using the lower estimate of  $Q_{\text{max}} \geq 90$  obtained for the 8/10 hetero-dimer, a rate constant for singlet-energy transfer of  $k_{\text{EN}} \geq 6 \times 10^{10} \text{ s}^{-1}$  is obtained, corresponding with a distance between donor and acceptor of  $\leq 17$  Å. Using molecular modeling a distance of 18–19 Å has been estimated between the center of the fullerene and the center of the first phenyl ring of the OPV unit, *i.e.* close to the estimate of 17 Å based on the Förster model. For covalently linked OPV4- $\text{C}_{60}$  we established that delocalization of the singlet-excited state onto the first benzene ring of the OPV4 unit is indeed a requirement to explain the high rate for singlet-energy transfer of  $k_{\text{EN}} = 5.3 \times 10^{12} \text{ s}^{-1}$  in this dyad by the Förster mechanism.

### 3. Acknowledgements

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### 4. References

- [1] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, *Science* 258 (1992) 1474; G. Yu, K. Pakbaz, A.J. Heeger, *Appl. Phys. Lett.* 64 (1994) 3422.
- [2] G. Yu, A.J. Heeger, *J. Appl. Phys.* 78 (1995) 4510; G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 270 (1995) 1789; J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, *Nature* 376 (1995) 498.
- [3] D.C. Sherrington, K.A. Taskinen, *Chem. Soc. Rev.* 30 (2001) 83; M.M. Conn, J. Rebek Jr., *Chem. Rev.* 97 (1997) 1647; C. Schmuck, W. Wienand, *Angew. Chem., Int. Ed.* 40 (2001) 4363.
- [4] F.H. Beijer, H. Kooijman, A.L. Spek, R.P. Sijbesma, E.W. Meijer, *Angew. Chem., Int. Ed.*, 37 (1998) 75; S.H.M. Söntjens, R.P. Sijbesma, M.H.P. van Genderen, E.W. Meijer, *J. Am. Chem. Soc.*, 122 (2000) 7487.
- [5] M.T. Rispens, L. Sánchez, J. Knol, J.C. Hummelen, *Chem. Commun.* (2001) 161.
- [6] E.H.A. Beckers, P.A. van Hal, A.P.H.J. Schenning, A. El-ghayoury, E. Peeters, M.T. Rispens, J.C. Hummelen, E.W. Meijer, R.A.J. Janssen, *J. Mater. Chem.*, 12 (2002) 2054.
- [7] W.L. Jorgensen, J. Pranata, *J. Am. Chem. Soc.*, 112 (1990) 2008; J. Pranata, S.G. Wierschke, W.L. Jorgensen, *J. Am. Chem. Soc.*, 113 (1991) 2810.
- [8] O. Stern, M. Volmer, *Phys. Z.*, 20 (1919) 183.
- [9] The supramolecular association of the donor and acceptor was also observed in a  $^1\text{H}$  NMR spectrum of a mixture of both chromophores.
- [10] In a 1:1 mixture of two compounds A and B, the statistical ratio for the formation of dimers is 1 : 2 : 1 for A-A : A-B : B-B.